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Structure - Property -Processing Relationships

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MOCVD OF TlBaCaCuO SUPERCONDUCTING THIN FILMS: STRUCTURE-PROPERTY-PROCESSING RELATIONSHIPS

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Superconducting TlBaCaCuO films were fabricated using a three step process. Amorphous BaCaCuOF films were grown on MgO(100) single crystal substrates by metalorganic chemical vapor deposition at 500°C and 4 torr using fluorinated β -diketonate complexes of Ba, Ca, and Cu. The fluorine was stripped in wet O₂ at 785°C and c-axis oriented Tl₂Ba₂CaCu₂O_x films were formed by annealing in dry O₂ between 850 and 900°C in the presence of Tl_xO_y vapor. The best films showed onsets of superconductivity at 125 K and zero resistivity was achieved by 109 K. Surface resistivities an order of magnitude lower than gold at 17 GHz (77 K) and J_cs as high as 10⁴ A/cm² (90 K) were obtained with unpatterned films.

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$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ has the highest T_c of all of the copper oxide superconductors and several phases of TlBaCaCuO are superconducting above 100 K. In addition, the high critical current densities (J_c) and extremely low microwave surface resistivities observed for polycrystalline TlBaCaCuO thin films [1] suggest that this will be the first HTSC materials system to reach commercial applications. Many of these applications will require uniform thin films and several methods have been used to deposit TlBaCaCuO . In all cases, post deposition anneals in Tl_xO_y atmospheres have been required to optimize the superconducting properties of the films. Results of YBaCuO and BiSrCaCuO thin film annealing studies [2,3] suggest that the quality of the post-annealed TlBaCaCuO films could be improved by proceeding through group II fluoride intermediates. A single report of this approach in which the precursor films were prepared by the e-beam evaporation of BaF_2 , CaF_2 , and Cu has appeared in the open literature [4]. Highly c-axis oriented $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_x$ films were obtained with T_c exceeding 104 K on $\text{MgO}(100)$.

In this study, the $\text{BaF}_2/\text{CaF}_2/\text{CuO}$ precursor films were prepared by MOCVD at 500°C and 4 torr in an inverted vertical stagnation point flow reactor. Barium and calcium 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-octane-4,6-dionate and copper hexafluoroacetylacetonate were used as the source reagents. Nominal growth rates of 0.2 microns/h were realized on degreased $\text{MgO}(100)$ single crystal substrates; the details of the growth system which gives uniform growth ($\pm 4\%$) over 7.62 cm diameter wafers are reported elsewhere [5,6]. Typical run conditions are given in Table 1 and the as-deposited films were an amorphous mixture of oxides and fluorides and found to be highly stable in air. The films were annealed in wet ($P_{\text{H}_2\text{O}} = 20$ torr) oxygen at 785°C to strip fluorine and complete fluorine removal (fig 1.) was verified with energy dispersive X-ray analysis (EDX). Thallium incorporation was carried out in a second annealing step in the

presence of $\text{Tl}_2\text{O}_3/\text{BaCaCuO}$ ($\text{Tl}:\text{Ba}:\text{Ca}:\text{Cu}$ cation ratio of 2:2:2:3) pellets. The $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ powder was first prepared by calcining $\text{Ba}(\text{NO}_3)_2$, CaO , and CuO (Aldrich Chemical Co.) at 890°C in flowing oxygen for 24 h [7]. The superconducting properties of the BaCaCuO thin films annealed in the presence of the pellets consisting of a physical mixture of Tl_2O_3 and $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ powder were superior to those annealed in the presence of stoichiometric $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ceramics. At the present time the detailed mechanism of Tl incorporation into the thin films is unknown; however, in the latter case the films were found to be Tl deficient as determined by atomic absorption analysis.

The post annealed films had a glossy metallic appearance. Typical surface morphologies of films annealed below 870°C consisted of rod shaped crystallites dispersed within a matrix of smooth continuous platelets (fig. 2). EDX analysis indicated that the platelets are Ca rich relative to the rod shaped crystallites. Increasing the annealing temperature to above 875°C increased the platelet dimensions to several tens of microns (fig 2.). The results of X-ray diffraction (XRD) analysis (fig. 3) suggest that the films are predominantly the 2212 phase with the c-axis oriented perpendicular to the substrate surface. In addition, more pronounced resistivity drops between 120 and 125 K were observed for films annealed at 875°C which reflects the contribution of the 2223 phase (fig. 3) to the electrical properties. These results are consistent with the recent report that annealing sputter-deposited TlBaCaCuO films at high temperatures (e.g., 900°C for 1 hr) gives films with sheet-type morphologies that are predominantly $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ [8].

The resistive transitions of the films was measured by a standard four-point probe method. The resistivity of the film shown in fig. 2b deviated from a monotonic decline at 125 K and reached zero at 109 K (fig. 4). The onset in the RF eddy current measurement coincides with the completion of the percolative

transition in the four point probe measurement (fig. 5). The breadth of the inductive transition suggests that the film is weakly linked and/or contains a distribution of phases with differing T_c s; either effect may be caused by the slight excess of Ca present in the films. The strong suppression of the critical current by a 800 Oe magnetic field applied parallel to the surface of the film but perpendicular to the direction of the current flow confirms that the film is weakly linked (fig. 6).

In general, Ca and/or Cu rich (relative to 2212) films showed a sharp drop in resistivity between 120 and 125K with the transition being complete by 105 ± 3 K (fig. 5). The films could accommodate Ca in excess of the 2223 stoichiometry and still exhibit superconducting transitions above 105 K (fig. 7); however, Ca molar ratios greater than 2 resulted in an increase in the normal state resistance and a decrease in the average grain size of the film (fig. 2c). Surprisingly, only one small peak ($2\theta = 27^\circ$) arising from a second phase appeared in the XRD pattern of the Ca rich films (fig. 3b); furthermore, the peak widths of the 2212 phase did not broaden relative to the nearly stoichiometric sample (fig. 3a). Peak broadening would be expected if the excess Ca occupied Tl lattice sites in the thin film. Although the syntactic intergrowth of the 2212 and 2223 phases implied by the XRD pattern in fig 3a does not allow a straight forward comparison; the XRD data are at least consistent with the interpretation that extensive substitution of Ca on Tl lattice sites does not occur. Tl-Ca site disorder has been observed in bulk ceramic and single crystal samples and has been shown to strongly influence T_c [9]. The decrease in the intensity of the peaks assigned to the 2223 phase in the XRD pattern of the Ca rich sample (fig. 3b) is in agreement with the report that Ca-vacancies are required for the formation of the 2223 phase [10].

The surface resistance (R_s) of the films was measured in a parallel plate cavity and the R_s of the best unpatterned films was approximately one fifth that of

a gold standard at 77K and 17.3 GHz. J_c s as large as 10^4 A/cm² (3 μ V/cm criterion) were reached by 90K in the unpatterned films which suggests that the actual values are much higher at lower temperatures. Detailed studies of the effect of the patterning on the superconducting properties of the films are in progress and the highest J_c s observed in patterned films have been 5×10^4 A/cm² at 4 K.

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TABLE 1. Deposition conditions for BaCaCuOF films.

O ₂ flow rate (sccm)	Ar flow rate (sccm)	Source reagent transport rate (10 ⁻⁶ mole/m)		
		Ba(fod) ₂	Ca(fod) ₂	Cu(hfacac) ₂
170	190 ~ 210	12 ~ 18	6 ~ 15	0.35 ~ 0.56

Fig. 1. EDX spectra (a) before and (b) after annealing in wet oxygen at 785°C for 1 h.

Fig. 2. Scanning electron micrograph of $\text{Tl}_2\text{Ba}_2\text{Ca}_{1.4}\text{Cu}_2\text{O}_x/\text{MgO}(100)$ after annealing at (a) 870°C and (b) 875°C and (c) $\text{Tl}_2\text{Ba}_2\text{Ca}_{2.3}\text{Cu}_3\text{O}_x/\text{MgO}$ after annealing at 875°C.

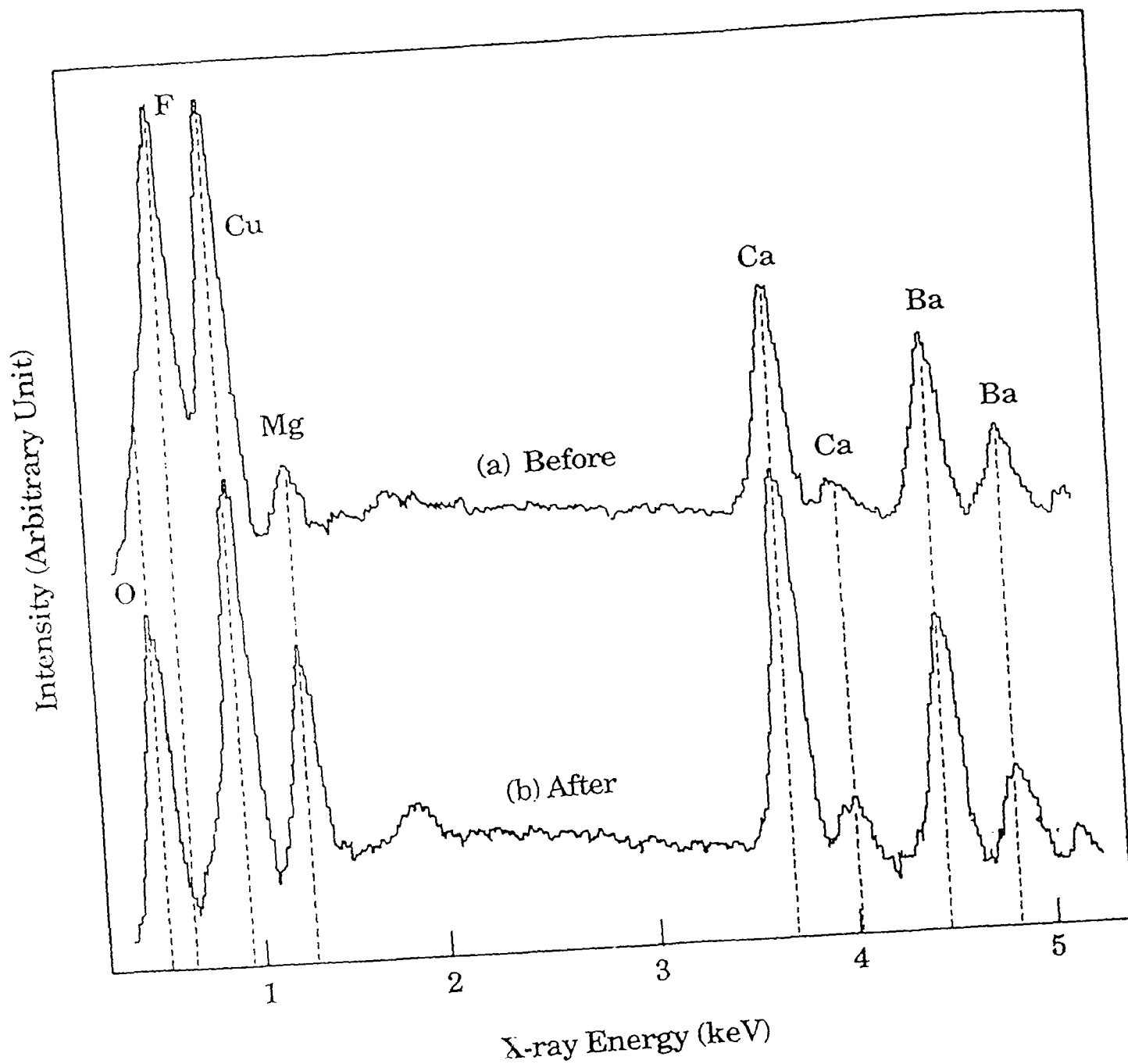
Fig. 3. X-ray diffraction pattern of (a) $\text{Tl}_2\text{Ba}_2\text{Ca}_{1.4}\text{Cu}_2\text{O}_x/(100)$ and (b) $\text{Tl}_2\text{Ba}_2\text{Ca}_{2.3}\text{Cu}_3\text{O}_x/\text{MgO}$ after annealing at 875°C; peaks assigned to the 2223 phase are labeled with a *.

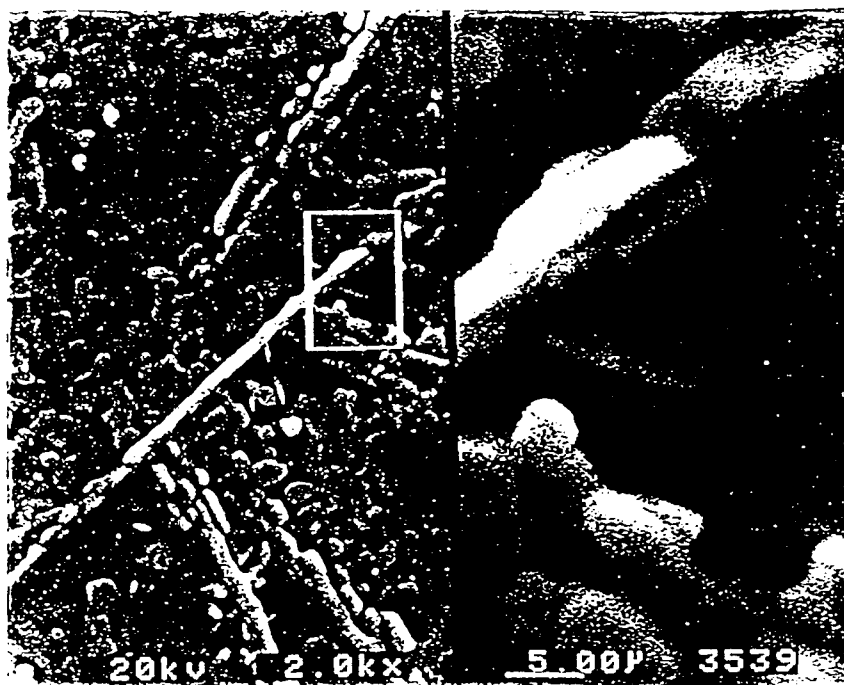
Fig. 4. Resistive transition of $\text{Tl}_2\text{Ba}_2\text{Ca}_{1.4}\text{Cu}_2\text{O}_x/\text{MgO}(100)$ after annealing at 875°C.

Fig. 5. Inductive transition of $\text{Tl}_2\text{Ba}_2\text{Ca}_{1.4}\text{Cu}_2\text{O}_x/\text{MgO}(100)$ after annealing at 875°C.

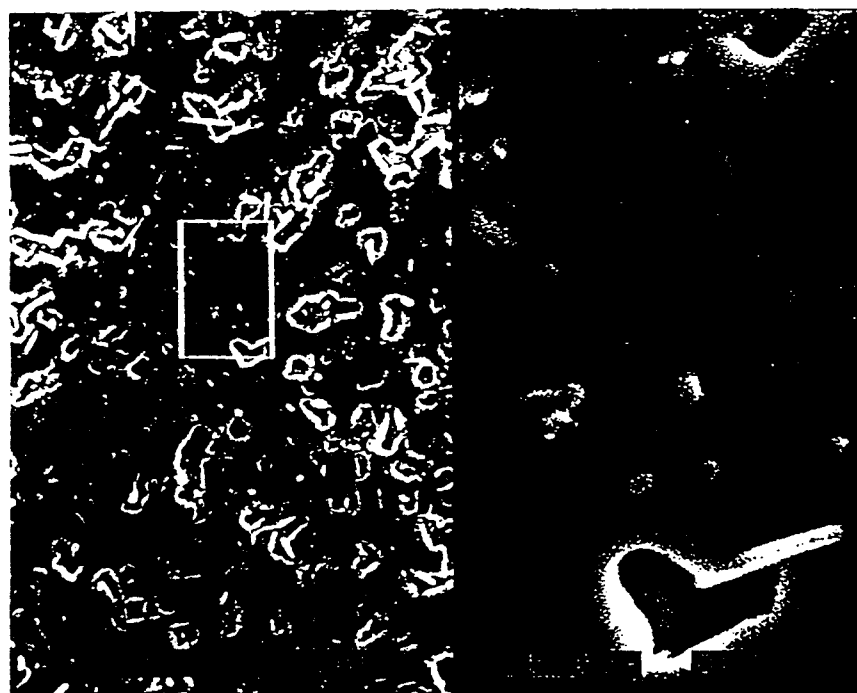
Fig. 6. Log-log V-I plot showing magnetic field dependence of I; the crosses and large diamonds are in zero field at 76 and 4 K, respectively and the small diamonds are in an applied field of 800 Oe at 76 K.

Fig. 7. Resistive transitions of TlBaCaCuO films on $\text{MgO}(100)$ with different precursor Ba:Ca:Cu cation ratios: (a) 2.0:2.57:2.67 and (b) 2.0:2.26:3.23

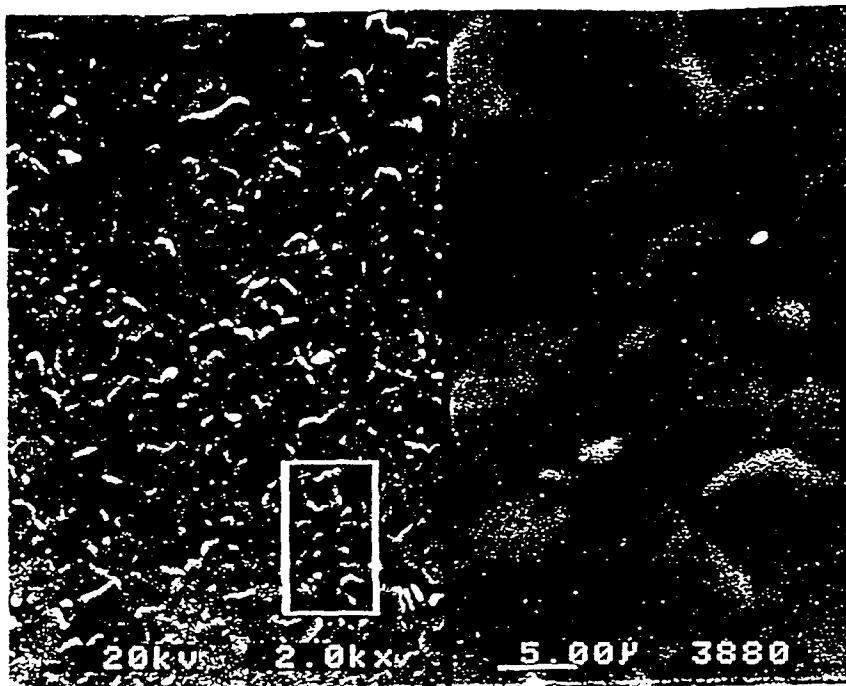




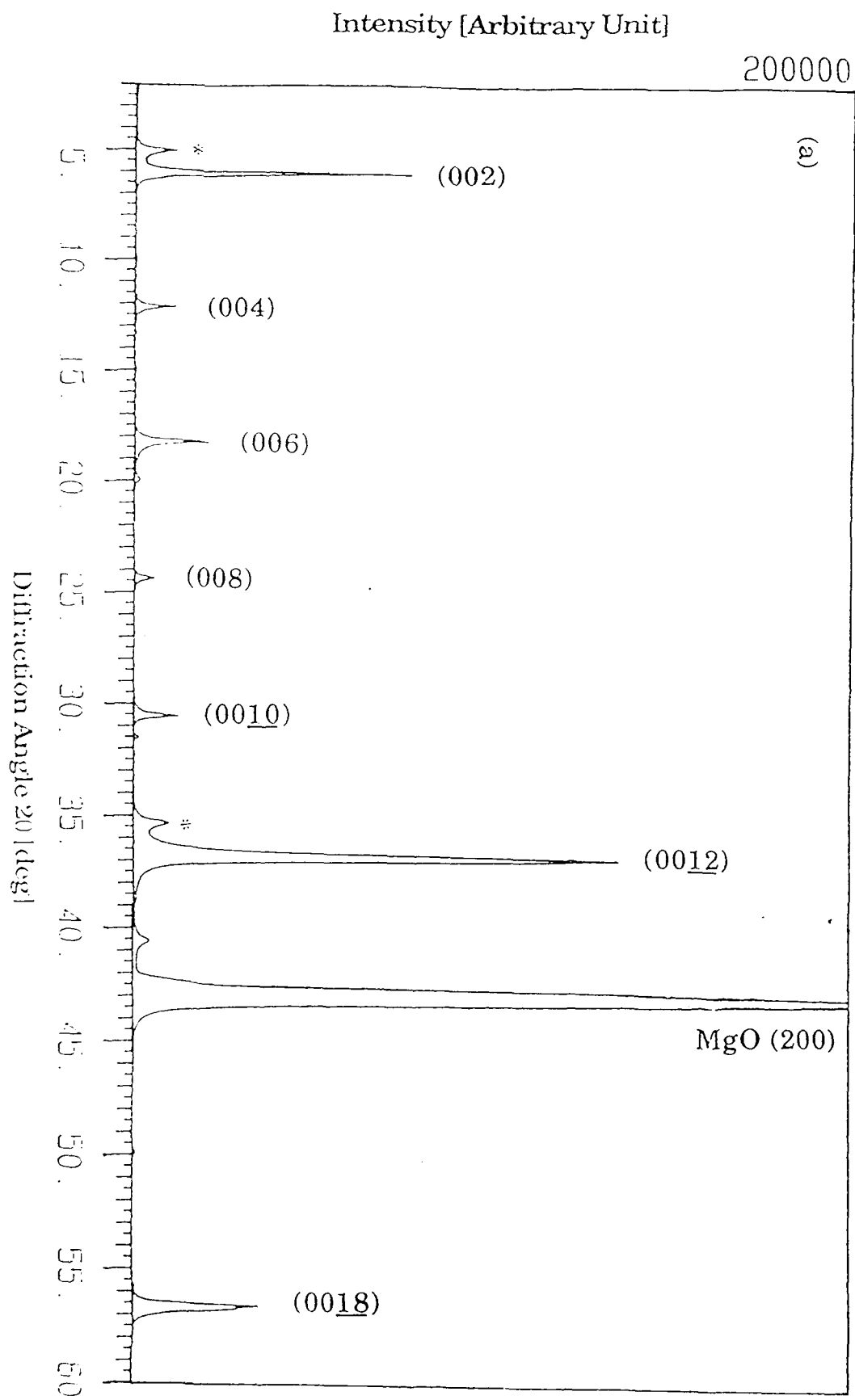
(a)

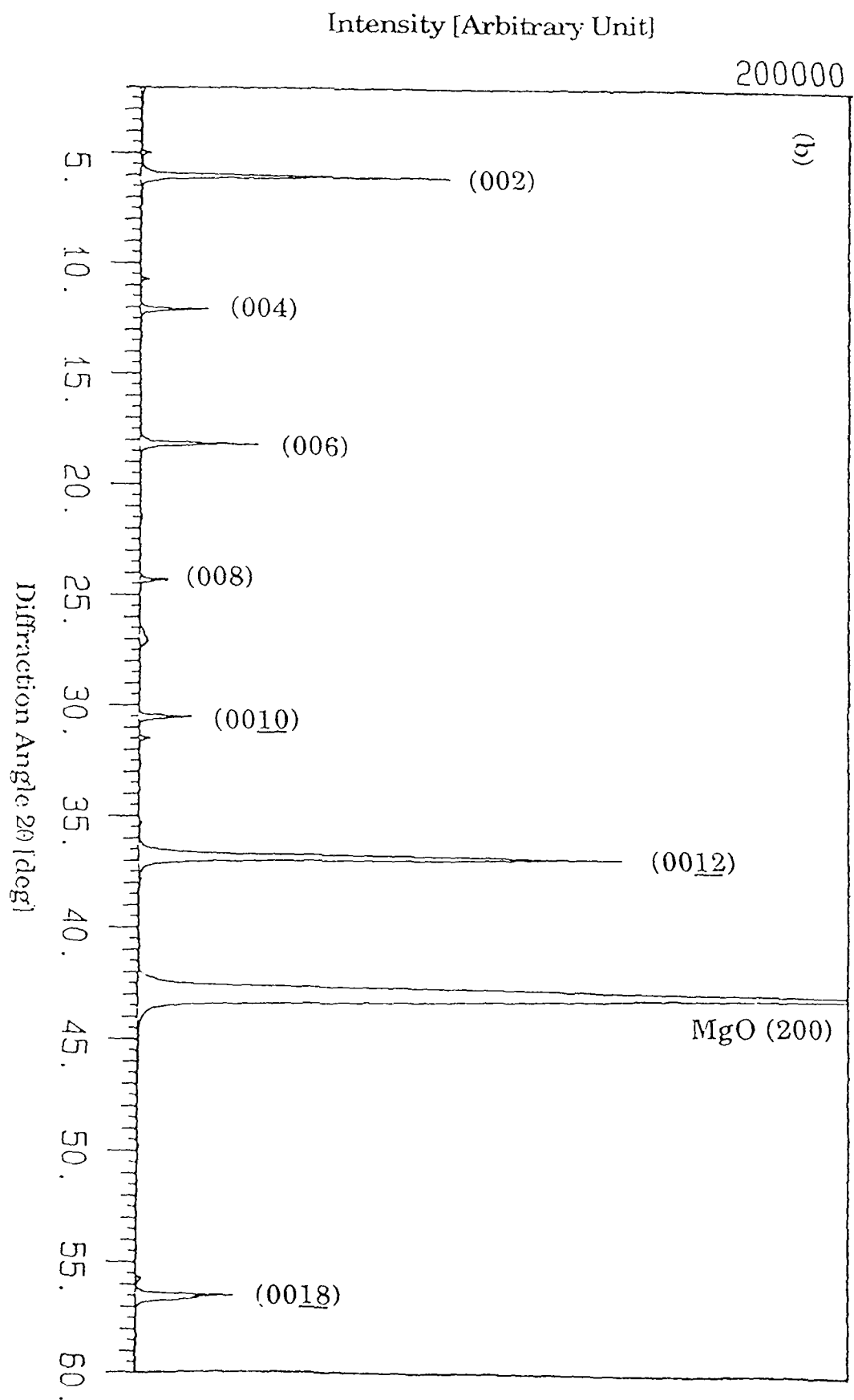


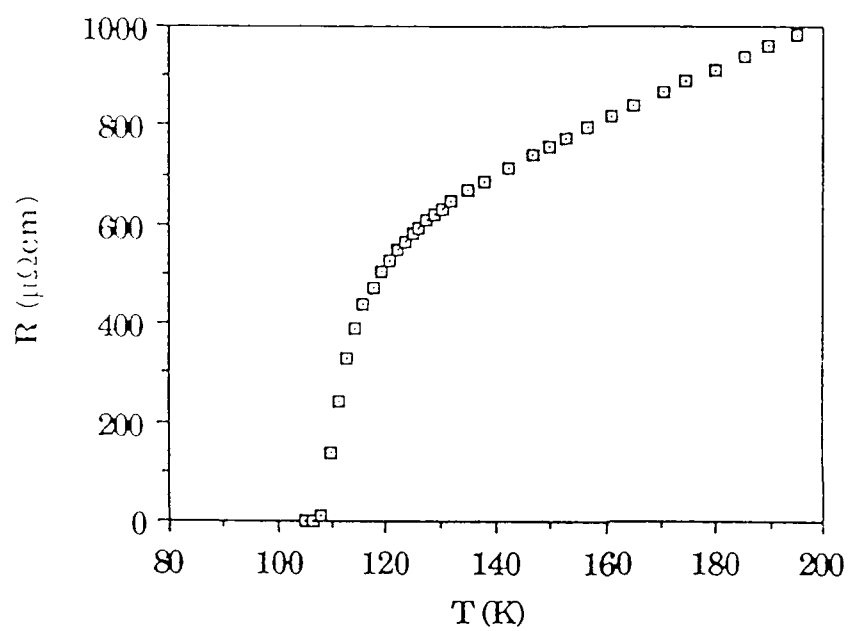
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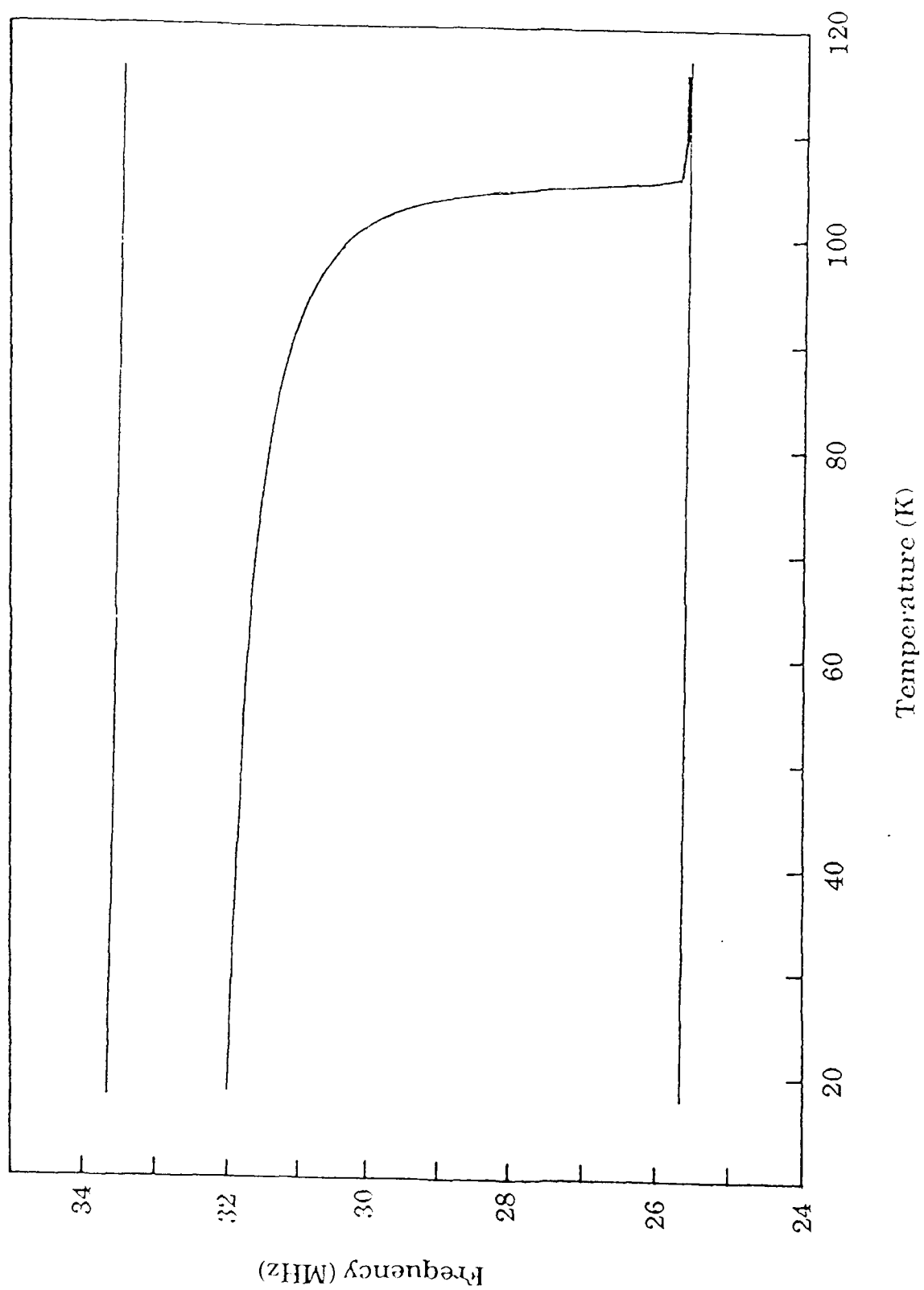


(c)









LOG V (LV)

